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by

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TABLE OF CONTENTS

ABSTRACT 1

I. INTRODUCTION 2

II. AUTOMATIC AIR SAMPLERS 4

A) Particle Size Separation 4
B) Sample Changer 7
C) Electronic Controller 9
D) Test Results 9

III. DIGITAL CODING 11

A) Design of the Code 11
B) Reading of Filter Labels 12

IV. BETA GAUGE 12

A) Design 13
B) Accuracy 15
C) Automatic Operation 17

V. X-RAY SPECTROMETER 17

A) Pulsed X-ray Tube 18
B) System Design 18
C) Test Results 19

VI. DATA REDUCTION 20

A) X-ray Fluorescence Analysis Programs 21
B) Beta Gauge Programs 21
C) Data Handling Programs 22

REFERENCES 25

FIGURE CAPTIONS 26

FABRICATION OF MONITORING SYSTEM FOR DETERMINING MASS AND COMPOSITION OF AEROSOLS AS A FUNCTION OF TIME

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ABSTRACT

This report describes the research and development efforts carried out during calendar year 1974 by the Lawrence Berkeley Laboratory under an interagency agreement between the ERDA and EPA. The program is a continuation and extension of earlier work in the development of instrumentation for air particulate sampling and analysis.* During the period covered by the report we have completed the design and construction of an integrated system for the automatic acquisition of air particulate samples collected in two distinct size ranges and have developed improved instrumentation for their subsequent analysis for total mass and elemental composition.

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* Earlier Progress Reports

F. S. Goulding and J. M. Jaklevic, "X-ray Fluorescence Spectrometer for Airborne Particulate Monitoring", Environmental Protection Technology Series EPA-R2-73-182, April 1973.

F. S. Goulding and J. M. Jaklevic, "Development of Air Particulate Monitoring Systems", Environmental Monitoring Series EPA-650/4-74-030, July 1974.

I. INTRODUCTION

Most of the emphasis of this year's program was concerned with the implementation of instrumentation based on earlier development work on X-ray fluorescence analysis with pulsed X-ray excitation, particle separation using the virtual impaction method, and total particulate mass measurements by beta-ray attenuation.[1] The goals were the construction of a complete aerosol analysis system based on the above techniques and its installation as a part of the St. Louis Regional Air Pollution Study.

The major effort in the first two-thirds of the year was devoted to the design, construction and testing of the Automatic 'Dichotomous' Air Samplers capable of separate collection of air particulate samples from the aerosol size ranges above and below 2 μm diameter on membrane type filters. The design of the sampler is based on earlier development work on the virtual impactor, but includes additional features such as automatic sample changing, automatic sequencing of sampling intervals and feedback flow control. The completed units have been delivered to the RAPS contractor in St. Louis and installed in ten selected locations in the Regional Air Monitoring Study (RAMS) network. These units are scheduled to begin continuous operation during the February 1975 intensive study period.

An advanced design X-ray fluorescence analysis system based on our earlier work,[2] including a high-rate pulsed excitation method[3] has been developed. The enhanced data acquisition rate achieved with such a unit results in a much reduced time required for the elemental analysis of the collected particulates. This is essential if we are to handle the large number of filters produced by the ten automatic air samplers.

The total particulate mass will also be measured in the laboratory using an automated beta-gauge. The computerized system is capable of measuring the weight per unit area of samples at a rate over 50 per hour to an accuracy of 10 $\mu g/cm^2$. The operating strategy will involve the mass measurement of blank filters before they leave the laboratory and a second measurement after they return from the remote sampling site and have been equilibrated at a standard relative humidity. The high throughput of the automatic beta-gauge like that of the X-ray analysis system is essential to the program.

An Extensive computer programming effort has gone into the problem of automatic sample handling, and data acquisition, storage and retreival. The handling of samples has been facilitated by the use of standard commercial photographic slide cartridges. All the automatic equipment used in the study has been designed to accept cartridges containing 36 samples, thereby reducing the handling of individual membrane filter samples with the associated possibility of damage or loss. Bookkeeping aspects of the data storage programs are simplified by the use of a digitally-coded and computer-readable label for each sample. The results of various measurements performed on a sample are always associated with this identifying number thereby reducing any possibility of confusion. The sample identity is also visually readable.

Figure 1 is a chart showing the flow of samples through the complete system as anticipated for the 1975 RAPS program. The input consists of individual sample holders each containing a membrane filter and identified by the computer-readable code. Present plans call for 1.2 μm cellulose membrane filters to be manufactured and mounted in the frames by the Nucleopore Corporation. Digital labels will then be attached at LBL.

The 5.08 x 5.08 cm filter holders are then loaded in the 36-sample cartridges and automatically beta-gauged to obtain the initial weight of the substrate. The filters are sent into the field where they are exposed on site using the automatic dichotomous sampler. Upon return to LBL they are again beta-gauged and the deposited masses are determined. X-ray fluorescence analysis is performed to measure the elemental composition. Data from these measurements are then entered into the main RAPS data bank where they can be associated with other measurements from the program. The analysis is non-destructive and the samples are available for examination by other techniques if needed.

The bulk of this report discusses in detail the various components of the system.

II. AUTOMATIC AIR SAMPLERS

The method of virtual impaction of aerosol particles investigated during the preceeding year was the starting point for the design of the dichotomous air samplers.[1] Further work carried out in this year has given us a much better understanding of the physical mechanisms involved in the virtual impaction method and resulted in improvements in the basic design. The following sections will contain a brief review of the principles of operation together with a discussion of our more recent work on virtual impaction. A detailed description of the automatic dichotomous samplers then follows.

A) The Particle-Size Separation

The size separation of aerosol particulates by impaction depends upon the relative balance between inertial and aerodynamic forces. In the conventional impactor shown in Fig. 2, a well defined air stream is caused to turn abruptly upon impingement against a flat plate. Whether particles entrained in the air stream strike the plate or not depends upon the relative magnitude of the inertial 'force' which tends to maintain a straight particle trajectory and the viscous drag force which tends to carry the particles along the air flow streamlines. Since the ratio of these two forces depends upon the particle diameter, we see that very large diameter (and mass) particles will strike the plate whereas very small particles will continue to follow the air stream. The particles collected on the plate would ideally consist of all sizes above a well defined cut-off diameter. In practice the characteristics are far from ideal due to the spacial variation of the streamlines and the effect of particles bouncing off the impaction plate (and reentering the air stream)

In the virtual impaction technique, the flat plate is replaced by a hole or tube leading to a region of relatively stagnant air and the impaction plate is simulated by a 'virtual' surface of streamlines.[4,5] Particles then impact through the surface into a region from which they are collected on filters. This has several advantages over conventional impaction:

i) The particles can be uniformly deposited on filters after separation, making an ideal sample for subsequent X-ray fluorescence analysis and beta gauge measurements.

ii) The phenomenon of particle bounce which plagues conventional impactors can be advantageously utilized to reduce losses within the virtual impactor.

iii) The problem of reentrainment is reduced to a second order effect since only the particles lost on the impactor walls are subject to blow off.

This basic idea has been expanded into a working device for the size separation of particles. Early experience showed that the method cannot operate with zero flow down the impaction tube but, instead, a small fraction of the incident flow must be drawn into the impaction volume to prevent turbulence in the particle separation region. This results in some contamination of the small particles in the large particle fraction. For this reason, the impactor has been designed as a two-stage device; the second stage removes more of the small particles from the large particle fraction. In order to achieve flow rates of 50 ℓ/min through the unit and still maintain the proper jet velocity and impaction stage dimensions necessary for the 2.5 μm cut point, it proves advantageous to make the first stage a three-parallel jet system while keeping a single jet for the second stage.

Further refinement to the design involved a study of the detailed particle size cut-off and loss characteristics for the individual virtual impaction jets. For this study an adjustable single jet/impaction tube was constructed and a series of measurements performed. The design of the final double stage, multiple jet unit was based on the detailed characterization of such a single jet.

Figure 3 is a schematic of a single jet virtual impactor indicating those parameters which would appear to be most important based upon our experimental and theoretical knowledge of conventional impactors.[6] Our approach to the present problem was first to discover those parameters which were least critical to the operation of the impactor and then to optimize with respect to the remainder. Performance criteria considered most important were the sharpness of the cut characteristic and losses as a function of particle size. The measurements were made using mono-disperse particles,

generated by a Berglund-Liu-vibrating orifice generator with fluorescent dye used as a tracer for subsequent quantitative analysis. This method is described in detail in last year's report.

Of the six variables D_1, D_2, S, Q_0, Q_1 and Q_2 shown in Figure 3, the parameters D_1 and Q_0 are more or less fixed by the design flow rate and cut point. They constitute what can be thought of as a characteristic length and flow. Experiments done by varying S/D_1 while observing the cut point showed the variation to be relatively small over the range $0.5 < S/D_1 < 2$. Similar measurements made varying D_2/D_1 showed minimum losses at $D_2/D_1 = 1.3$.

The flow division Q_1/Q_0 (or equivalently Q_1/Q_2) should clearly be as small as possible for each stage since this ratio is porportional to the contamination of small particles in the large particle fraction. However, at small values of Q_1/Q_0, there appears to be significant turbulence in the impaction tube which results in high particle loss and size mixing. The amount of cross contamination of 10 μm particles into the small particle stream was taken as an indicator for turbulent mixing. It was found that a ratio of $Q_1/Q_0 > 0.15$ was necessary to prevent sizeable cross contamination. Based on these measurements, with further considerations on the detailed shape of individual jets, flow symmetries, mechanical integraties and ease for servicing, an optimized design was developed. A cross section of the final design is shown in Fig. 4. The first stage consists of three single jets arranged in a symmetric circular pattern. The individual jet shapes can be seen in the parts labeled 1 and 4. The parameters for each first stage jet are as follows:

$D_1 = 3.86$ mm, $D_2 = 5.05$ mm, $S = 3.81$ mm, $Q_0 = 16.7$ ℓ/m, $Q_1/Q_0 = 0.25$.

The combined flow Q_1 from all three jets is now 12.5 ℓ/m and contains all of the large particles plus 25% of the small ones. This flow goes through a tapered, vertical drift space to a second stage where the flow is again divided. The second stage parameters are:

$D_1 = 2.87$ mm, $D_2 = 3.86$ mm, $S = 3.18$ mm, $Q_0 = 12.5$ ℓ/m and $Q_1/Q_0 = 0.20$.

The combined outputs consist of the 2.5 ℓ/m fraction on filter A with all the large particles and 5% of the small ones, and filter B with 95% of the small particles.

Figure 5 shows the final performance curves for the impactor. The results show a greatly improved performance over the device previously evaluated.[1] Assuming that loss components are proportional to the collected size fractions, the collection efficiency for filter A will be A/A+B and has its 50% point at 2.5 μm Stoke's diameter (or equivalent diameter of a unit density sphere). The cut characteristic is sharper and the losses are greatly reduced relative to the previous design. The losses observed with liquid particles are considerably higher than those obtained for solid particles due to the increased sticking probability and should be considered a worst case estimate since typical particulates are most often solid in nature. Note that the occurance of the loss peak near the cut point corresponds to the inevitable probability for particles in the transition size region to come into contact with the physical surfaces which shape the necessary streamlines. It is fortunate that such a loss peak generally coincides with the minimum of a typical bimodal urban aerosol size distribution. We have operated these samplers continuously for 6 to 8 weeks without significant change in performance.

All of our objectives have been realized in the design which appears to be superior to conventional impactor designs in all respects. Another obvious advantage is that the size-separated particles are suspended in gas flows that can be piped to any instrument downstream. The virtual impactor can therefore be used as an input stage for any type of particulate measurement where size segregation is desired.

B) Sample Changer

The St. Louis RAPS air particulate program requires total mass and elemental composition measurements to be performed on deposits on membrane-type filters. The automatic sampling of the two size ranges means that the blank membrane filters must be presented to the device in pairs in a predetermined time sequence. The automatic sample changer and associated electronic controller are designed to do this.

Our design for the complete sampling/analysis cycle is oriented toward the use of discrete 37 mm diameter membrane filters which have been mounted on 5.08 x 5.08 cm (2" square) plastic sample holders. These samples in turn are mounted in standard 35 mm plastic projector cartridges capable of holding up to 36 slides in a linear array. These are then loaded as a unit into either the sampling equipment or analysis system. Advantages of this approach include commercial availability of the cartridges and reduced manual handling of the individual samples.

The automatic sample changer is designed to accommodate two cartridges at the same time--one for each size range. The sequence of events involved in changing filter samples then proceeds as follows: Slides from each cartridge are extracted, placed in the sampling region and clamped to provide an adequate vacuum seal. Air is then pumped through the filters via the virtual impactor for a predetermined time interval--typically 2 to 24 hours--in order to accumulate the air particulate sample. At the end of this time samples are unclamped and returned to the cartridges; then the cartridges are advanced one increment to select the next pair of filters.

In the sampling station design, these mechanical functions are performed using a reciprocating motion similar to that in certain types of conventional slide projectors with the addition that the samples are mechanically clamped in the inserted position. Figure 6 is a schematic diagram of such a system. The component termed 'Geneva Wheel' refers to the vertical cartridge increment mechanism which is actuated by the return motion of the horizontal shuttle.

Also shown on the diagram are pressure sensors P_0 and P_1. The differential pressure P_0 is the drop across the fixed impedance of the virtual impactor and is used as an indicator of total flow. Since the operating characteristics of the virtual impactor depend critically on the internal flow conditions, a feedback loop actuating a variable orifice valve is used to maintain a constant flow independent of variations in filter impedance either from filter to filter or during the course of a run as the loading increases. The sensor P_1 is used to detect an improper vacuum seal on filter A or a broken filter. With the present set up, P_1 actually monitors filter B as well since the vacuum for the fixed limiting orifice depends upon proper flow condition in the fine particle stream.

Since a remote sampling station must be more reliable than a typical laboratory instrument, the sample changer has been designed with these considerations in mind. The prototype has been thoroughly tested for reliability with satisfactory results. Provision has also been made for the monitoring of possible mechanical failures by the central control computer.

C) Electronic Controller

The sequencing in the automatic sample change, the timing of sampling intervals and the status communications with the central computer facility are carried out in a single electronic control module. The unit is designed to operate semi-automatically with an interval clock for timing the samples, or it can operate under computer control from a remote location. As mentioned earlier, an automatic feedback loop maintains constant air flow rate.

Since the unit is designed to operate remotely, conditions resulting from malfunctions which might cause damage to the unit or invalidate a sample are monitored. Depending upon the magnitude of the problem the unit can be shut down to await corrective action on the part of the operator. A battery supply is included to maintain the control logic in the event of momentary ac power failure.

D) Test Results

The sampling characteristics of the completed units have been carefully measured in the manner discussed above and conform to the curve in Fig. 5. Of more general concern are the accuracy and reliability of the complete automatic air sampling system in a realistic experimental program. This requires that the quantity of air sampled be accuractely controlled and that the actual parcel of air sampled be truly representative of the ambient.

The accuracy in measurement of the quantity of air pumped through the sampler is dominated by the precision with which the constant flow can be maintained. The feedback loop employed in the present design adjusts the flow to maintain the pressure drop across the virtual impactor constant to

within one percent. To a first approximation this constant pressure drop leads to a mass flow which is inversely proportional to the square root of the absolute temperature and a volume flow proportional to the square root of absolute temperature. The samplers were calibrated at 20°C. The effect of temperature variation on the cut point will be small since the ratio of jet velocity to viscosity is relatively insensitive to temperature changes.

A serious consideration in the performance of the flow controller is the increase of filter impedance due to particle loading. The increase in impedance is automatically compensated by movements of the variable orifice valve, but excessive impedance in a given filter results in the flow control system running out of range. For the 1.2 μm pore cellulose membrane filter now used, the flow control range permits about a 70% increase in a filter impedance. For the small-particle size fraction (< 2 μm), this corresponds to a particle loading of approximately 200 $\mu g/cm^2$ on filter B. Since only 5% of the flow is drawn through filter A, it practically has no filter impedance limitations.

The question of whether the air flow entering the impactor adequately represents the ambient atmosphere is governed mainly by the coupling of the virtual impactor inlet to the outside air. Within the impactor itself the efficiency and loss curves show that below 10 μm particle diameter most of the particles at the inlet are collected on the filters. The upper particle size cut-off is around 20 μm where losses for liquid particles rise sharply to 70%.

The reliability of the completed air sampler has been extensively checked under laboratory conditions by continuously recycling 12 samplers over an extended period. The equivalent of 15,000 samples have been run as a part of this study. After elimination of some obvious failure modes early in the study, the average failure probability was reduced to less than 0.1% per sample. This converts to an average failure rate of once every 50 days per sampler when operated on a one-hour per sample cycle time. For 24 hour samples, the average rate should be less than once per year.

The 12 samplers have been delivered to the EPA/RAPS contractor in St. Louis and have been installed in the RAPS stations and initial start up tests have been performed. Full scale operation should occur by April 1, 1975.

III. DIGITAL CODING

Since the start of our program, a feature incorporated into our thinking about large-scale sample-handling has been the potential for labeling the individual membrane filter holders with a computer-recognizable identifying code. The original design of the 5.08 x 5.08 cm plastic filter holder included a region for some type of labelling.

A) Design of the Code

Considering the anticipated throughput of samples through the analysis facility, it is evident that a computer-readable label must be devised. While we were considering various methods for generating computer-readable codes, optically readable labels became commercially available. While these labels were designed for labeling and pricing of merchandise, discussions with representatives of the manufacturer led us to adapt the technique to our purpose. The coded labels are manufactured by Monarch Marking System, a Division of Pitney Bowes.

The labels consist of 38 x 9 mm adhesive paper with a 15 x 4 mm digital bar code. A duplicate printing of the number in ordinary numerals is also included. The individual characters consist of seven binary bits written at a density of thirteen characters per inch. The value of the bits is determined by the width of either the black line or white space. A wide line or space is 1, the narrow line or space is a 0.

Scanning of the code is performed by a light pen and interpretation of the pen output is performed in an electronic decoder supplied by the manufacturer. The output of the decoder is fed to a computer. The light-pen scan can be performed in either direction along the length of the label at any speed in the range 10 to 75 cm/sec. The code includes internal error checks which insure reliability of the encoder output; in the event of an inconsistent answer no output is produced.

B. Reading of Filter Labels

Labels are printed on two different colored substrates; numbers 0 to 49999 are printed on white paper and are intended for use with the large particle fraction; the yellow labels 50,000 to 99,999 are intended for use with the small particle fraction. These labels are normally attached to the filter after the filters have been mounted, but before any initial measurements are performed. All subsequent data on the particular filter will be associated with this unique sample number.

Scanning of the label is performed by a simple mechanism attached to the sample changer associated with the analysis equipment. When the filter to be analyzed has been removed from the cartridge and advanced to a predetermined position, the light pen is moved back and forth across the label at the appropriate speed and the result recorded. If no valid record is obtained, the filter is advanced by small increments and further attempts are made. If the label is not read in five attempts the identity of the sample can be ignored or extrapolated from the numbers of previous slides.

Extrapolation is useful in a large program, since the proper sequence of numbers can be maintained even if a particular label is somehow rendered illegible. That sample need not be eliminated from the study, it acquires an identity by its position relative to other samples in the stack.

IV. BETA GAUGE

A measurement of the total mass of the collected particulates is an important part of the aerosol monitoring program. X-ray fluorescence analysis is only sensitive to elements with $Z > 12$, and a large fraction of the particulate mass is composed of hydrocarbons and light elements. The conventional method for determing total particulate mass consists in sampling large volumes of air through a filter and gravimetrically weighing the accumulated deposit.

This approach is hardly practical for very large numbers of samples. A two-hour sample using the dichotomous sampler corresponds to 6 m^3 of air volume or 100 to 1000 µg of particulate deposit for typical conditions. To measure this mass accurately on large quantities of filters, particularly those mounted in the plastic holders, is virtually impossible using the conventional weighing method. Beta-gauging appears to overcome these objections and has been adopted in this program.

A) Design

The operation of a beta-gauge depends on the effects of electron energy loss on a continuous beta-ray spectrum from a radioisotope source when the electrons pass through a thin filter. Figure 7 shows an idealized beta-ray spectrum from a typical source measured with an energy-sensitive detector. In a typical beta-absorption measurement, all events whose energy is above a discriminator level are counted as a function of the total mass inserted between the source and detector. The electrons emitted from the source undergo interactions within the absorber resulting in a modification in the electron distribution. The effect of absorption by a thin specimen on the continuous beta-spectrum is a complicated problem theoretically, since each energy of electrons undergoes an energy loss proportional to the thickness of the specimen, but depending in a more complicated way upon the energy of the incident electron and the number and ionization energies of electrons in the absorber. This results in a downward shift of all electron energies shown in the spectrum of Fig. 7 by a variable amount. Experimentally the net effect of the absorber is to reduce the counting rate above a discriminator threshold according to an exponential law. This is

$$N = N_o e^{-\mu x}$$

Where N represents the counting rate measured, µ is an emperical mass absorption coefficient commonly measured in cm^2/gm and x is the thickness of the specimen in gm/cm^2.

A beta-gauge consist essentially of a radioactive source and associated detector arranged in a fixed geometry. The appropriate source for a given problem depends on the range of masses over which the system is required to operate. As a general rule, the end-point energy of the beta spectrum should be proportional to the mass range considered. For optimum sensitivity the energy should be as low as possible consistent with the fact that a statistically significant number of electrons must still have a range which exceeds the thickness of the maximum thickness absorber. Estimate of the mass absorption coefficient can be made based on empirical evidence.[7] In the present design, a ^{147}Pm source with E_{MAX} of 225 keV is used corresponding to an end-point electron range of approximately 60 mg/cm^2. This is appropriate for the 4 mg/cm^2 filters used in the study.

Figure 8 is a diagram of the beta gauge assembly. The detector is a 2.5 cm diameter lithium drifted silicon detector* contained in a vacuum cryostat which is then firmly mounted to a yoke which references it to the source assembly. The source assembly is also mounted in a vacuum chamber thereby allowing a long path from source to detector to provide uniform radiation of the filters without the effect of accompaning air absorption. Using a 500 μC ^{147}Pm source our counting rate is 20,000 cts/sec with no sample in position.

The design goals for the beta gauge system was an accuracy of 10% in the measurement of 100 μg/cm^2 deposit (i.e. ± 10 μg/cm^2). This represents an accuracy of ± 0.25% when referred to a total mass of filter plus deposit of 4 mg/cm^2. To highlight the precautions required in order to achieve this accuracy, we have calculated the sensitivity to various parameters in terms of a ± 10 μg/cm^2 equivalent effect on the final answer. Thus, a 10 μg/cm^2 change in output is equivalent to:

i) A change in barametric pressure of 1% over the 1 cm air path length.

ii) A change in detector to source distance of 0.0014 cm.

iii) A change in amplifier gain or discriminator setting of 0.1%.

iv) The statistical counting accuracy requires the total number of detected electrons be greater than 10^6 for each determination.

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* Note that this is not the type of detector that might be chosen for a general-purpose beta-gauge, but the detector system was readily available to us to use for this purpose.

These results show the extreme level of care required if this accuracy is to be achieved in the final mass measurement.

B) Accuracy

The practical accuracy and stability of the beta-gauge hardware was checked using uniform thin film standards. Calibration curves obtained over the range from 1 to 10 mg/cm^2 showed considerable departure from a simple exponential. A part of this departure could be attributed to electronic pile-up losses at the higher counting rate, lower mass end of the curve. However, no serious attempt was made to reconcile this non-exponential behavior since the theoretical considerations do not appear to warrant it. Instead, we realize that the measurement of importance concern the detection of 1 mg/cm^2 on less change in mass in a total mass of 4 to 5 mg/cm^2. By limiting our calibrations to a range of between 3 and 6 mg/cm^2 a reasonable fit to pure exponential behavior could be obtained.

Table 1 shows a summary of a typical calibration run. The calibration curve was obtained by a linear least squares fit of the logarithm of the count as a function of sample mass. Assuming a relationship of the form:

$$N = N_o e^{-\mu x}$$

then the fitted values are N_o = 4303976 counts/100 sec; and μ = 0.144743 cm^2/mg. The RMS deviation in Table I is 5.7 µg/cm^2. Examination of repeated calibration runs showed a consistent systematic deviation of certain standards from the exponential behavior. If an average of these deviations was obtained and then used to correct the individual input masses used in the exponential least squares fit, then a RMS deviation of 1.3 µg/cm^2 is achieved. This procedure can be justified in the present method of analysis since the absolute mass of the filter is less important than the difference in masses between successive weighings.

The stability of the calibrated instrument is approximately ± 0.25% (in total mass) over a period of two weeks; short term stability is much better than this. Since calibration of the instrument requires less than one half hour of running time, it is not unreasonable to calibrate twice per day, and achieve the desired accuracy.

Although the basic accuracy of the instrument has been shown to meet requirements, mass measurement of actual filters introduces additional potential errors such as the change in filter mass as a function of relative humidity. Measurements on several types of filters have shown that the necessary accuracy can be maintained by either equilibrating the filter at a standard relative humidity, or in the case of blank filters, by applying a correction factor which depends on relative humidity. The latter method is suspect in the case of filters which have collected ambient aerosols since the hygroscopic properties may then be dominated by the chemical form of the particulate deposit.

An additional parameter which may affect the final answer is any dependence of the beta-gauge result upon the average atomic number of the material being measured. To a first approximation, μ would be proportional to the number of atomic electrons per unit volume or Z/A. Since this ratio remains fairly constant for elements, with the exception of hydrogen, only a small dependence would be expected. However, various groups have observed dependence of beta-gauging results on the Z.

Figure 9 shows the results of beta-gauging samples having four different atomic numbers. The samples were in the form of thin (~ 1 mg/cm^2) evaporated deposits on 4 mg/cm^2 substrates. The curves show that the effect is quite significant causing errors of 30% or more for the case of Z/A = 0.40 (Au) compared to Z/A = 0.53 (polycarbonate). The fact that the observed absorption coefficient μ increases with decreasing Z/A reflects the effect of large angle scattering which is more pronounced for low-energy electrons in high Z materials.[8] However, if we assume that the majority of the mass consists of hydrocarbons and light elements, the range of Z/A is restricted to about 0.50 to 0.55 and the errors become less than 10%. Therefore, the effect probably does not seriously affect the accuracy of the method for air pollution application, but it does limit the more general applicability of the beta-gauge method for mass measurements.

C) Automatic Operation

The basic beta-gauge design has been adapted to operate with a sample changer similar to that used in the automatic dichotomous sampler. The design includes the capability for recording the digital code identification on the individual samples. The operation of this unit is controlled by the same Texas Instrument 960A computer as controls the X-ray elemental analyzer, and data are written on magnetic tape in the form of counts per sample. The initial mode of operation provides for the calibration curve to be generated off-line and applied to the output data in an off-line computer. Later versions will perform all of these operations in the Texas Instrument 960A computer. A more complete discussion of the overall data handling aspects is contained in Section VI.

V. X-RAY SPECTROMETER

The pulsed X-ray tube X-ray fluorescence spectrometer built during the past year is an improved version of the earlier type of spectrometer constructed in 1972. The previous unit has been operating successfully at Research Triangle Park since April 1973. The main advantages of the new design will be faster analysis by virtue of the increased counting-rate capabilities achieved with the pulsed excitation and the new sample changer which will accommodate the 36 sample cartridges used in the automatic dichotomous sampler.

A) Pulsed X-ray Tube

The design of the pulsed tube is basically the same as that described in an earlier report. Modifications to the high voltage cable have permitted the installation of the pulsing circuits in the oil-filled high voltage supply tank thereby eliminating the cumbersome housing which was formerly attached to the rear of the tube. It also eliminated high voltage breakdown problems which formerly limited the tube operation to less than 50 KV.

Figure 10 is a schematic of the complete X-ray tube-spectrometer control loop. It is a more detailed version of the control circuit schematic previously published in last year's report and also includes the computer control and protective circuitry as well as a more detailed presentation of the dead time correction for the current integrator. The integrated current output is corrected for those events where a coincidence between the central region and the guard ring causes a rejection of the pulse from signal processing and analysis. The output of the current integrator is utilized either by the computer, or a manual preset scaler, to control the analysis interval.

A modified anode structure has been installed in the tube in order to permit a much closer tolerance to be maintained in this critical area than in our earlier design. It also allows better air-cooling to dissipate the 100 watts of anode power.

B) System Design

The X-ray fluorescence system is similar to that built earlier with the exception of the pulsed X-ray tube, and improved X-ray tube-secondary target sample geometry. The secondary targets will be Cu, Mo and Tb as in our earlier work.

The sample changer has been completely replaced with a version capable of accommodating the 36 slide cartridges. Provision for reading the digited bar code is also included. As in the previous design, the system can be operated under computer control or in a manual mode if only a few samples are being analyzed.

C) Test Results

The operation of the pulsed X-ray system differs from that of a conventional X-ray fluorescent spectrometer in the manner in which the beam current and count rate are allowed to vary under the control of the automatic feedback loop. Figure 11 is reproduced here from last year's report. It shows the response of the system to varying sample masses under typical operating conditions. Curves A and B represent the pulsed power under the conditions indicated on the figure. We are most interested in the curves labeled 'average power' and 'counting rate'.

The feedback loop is designed to operate at the maximum allowable average power whenever possible when the sample mass is below about 4 mg/cm^2. The power limit is set by the anode dissipation capability which is 100 watts in the present air-cooled system. If the mass of the sample increases to where the maximum permissible count rate can be achieved, then the power is gradually reduced to maintain this count rate while still preventing excessive pileup. The maximum allowable count rate is the reciprocal of the pulse processing time. In the present system, the time is of the order of 50 μs and the maximum allowable counting rate is 20,000 counts/second.

However, it requires a finite amount of time to shut the tube off following an event in the detector. There is a practical upper limit on the counting rate dictated by the pulse pileup probability during this 200 ns interval. For this reason, when the sample mass is above 4 mg/cm^2, the minimum duty cycle detector indicated in Fig. 10 is used to maintain the X-ray tube power at a maximum level consistent with a tolerable pileup probability. This limits the average output counting rate to about 12,000 cts/sec corresponding to a 4% pileup probability in the output spectrum.

With the tube operated in this mode, the detectability curves shown in Fig. 12 were obtained. The vertical axis gives the 3 σ detection limits for the various elements assuming a 4 mg/cm^2 filter of the type used in the dichotomous sampler. The three curves correspond to the three fluorescers Cu, Mo and Tb. Curves b) and c) were measured with the new system, curve a) was extrapolated from earlier measurements using a conventional tube. Due to the operating mode of the pulsed tube, these detectable limits are

expressed in terms of ng/cm^2 per 20,000 dumps of the X-ray tube current integrator. This corresponds to 0.155 Coulombs of charge flow in the X-ray tube. Assuming a maximum anode power dissipation of 100 watts and a sample mass just below that required for maximum counting rate, Table II shows the amount of time required to achieve the sensitivities shown in Fig. 12. These numbers are subject to some variation as the total sample mass varies about the pileup limit, but are adequate as an indicator of the enhanced speed capabilities of the pulse-tube system.

VI. DATA REDUCTION

Computer programming efforts were divided among a number of various projects during this contract period. The major projects were the following:

i) Development of control programs for the pulsed X-ray tube analysis system and the automatic beta gauge. This included the facility for interpreting the digital label code on the individual samples.

ii) Modification of the existing X-ray spectral analysis program to interpret data from the pulse tube system and apply appropriate corrections for particle-size effects encountered in the dichotomous samples.

iii) Development of the beta-gauge data acquisition and analysis program.

iv) Development of programs to merge the data from the various sources into a single record for each sample.

v) Design a data handling strategy appropriate for interfacing with the RAPS data bank.

The last two items overlap somewhat with our 1975 program, but since they were anticipated in the 1974 program, they are discussed briefly here.

A) X-Ray Fluorescence Analysis Programs

The control program for the X-ray fluorescence unit was rewritten in order to accommodate the modified operating modes brought about by the new sample changer design, digital label reading and pulsed-tube operating characteristics. In addition to providing for the usual mechanical sequencing of events in the sample changer and digital reader, the new program serves as the controller for many of the data acquisition parameters including selection of fluorescers and live current intervals.

This program also provides the main entry point for all ancillary data on a given sequence of samples. Data such as site number, running time, and particle size range are entered from the teletype keyboard at the beginning of the analysis of a series of samples. This data then becomes associated with sample identifying numbers as read from the digital code. Subsequent handling of data can then be based on this information.

The spectral analysis program has been modified slightly to provide more convenient operating features and to correct a deficiency in the error calculations used previously. The corrections for particle size effect and interelement interferences will be handled in a separate program operating in the CDC 7600 computer. Particle size corrections will be treated separately for each size range using the values quoted by Dzubay.[9]

B) Beta Gauge Programs

The control program for the beta-gauge operates the automatic sampler, interprets the slide identifiers, and writes the output data on tape. The calibration of the beta gauge data is performed off-line on the CDC 7600. The calibration standards are identified by this program by their sample number and automatically update the internal calibration curve using a least squares fit to an exponential curve as discussed above. Subsequent data are converted from the number of counts to the mass in ng/cm^2 using this fitted data.

Since the final output data consists of a mass difference for a given sample before and after exposure to the particulates, the data from two separate measurements must be combined. The sequence of analysis in the beta-gauge will not be the same for the two sets of measurements. This requires a further merging operation of the two data outputs in order to arrive at the final answers. This again is accomplished off-line on the larger computer. The output of this program will be a sequentially numbered array of sample numbers, mass measurements before and after exposure, and the mass difference with associated error.

C) Data Handling Programs

Programs are being designed to merge the X-ray fluorescence data and beta-gauge results with the additional data concerning sampling conditions.

The sample handling strategy has been designed to include as much information as possible on the cartridge labels. When the cartridges are returned to LBL the labels should contain information concerning the sampling site identification, first and last sample numbers, the initial time of exposure of the first sample, and the interval between samples. The size range sampled is identified by the color of the label and the range of the sample numbers. This information should be adequate to specify the chronology of sampling. In the event of a break in the sample acquisition, there will be a back-up log book to enter such information.

This data will be entered into the system at the time that the samples are introduced into the X-ray fluorescence analyzer. The output data for each sample from the X-ray analyzer will then consist of the sample number together with all of the above sampling information. There will follow the block of elemental analysis results consisting of a list of elements and their concentrations with errors. A space in the output file will be left for the total mass as measured in the beta gauge.

This output tape will then be processed off-line and the appropriate particle size and interelement corrections will be applied. A subsequent merging operation will add the beta gauge results associated with that sample number to the output file.

Since this data will be ordered according to the sequence in which the cartridges are presented to the analyzer facility they have no relationship to the sampling sequence. A separate ordering operation will be performed off-line to sequence the data files in the order in which the samples were taken. A possible output magnetic tape would then consist of the time sequenced data for a given sampling site. The two size ranges will be listed in adjacent blocks for easy access. This data will be transmitted to the RAPS data bank in this form.

TABLE I

N (Counts/100 Sec)	A Mass From Fitted Curve (mg/cm^2)	B Gravimetric Mass (mg/cm^2)	Difference (A-B) ($\mu g/cm^2$)
2779527	3.0487	3.0443	4.4
2535370	3.6821	3.6827	- 0.6
23315 5	4.2596	4.2698	- 10.2
2124290	4.9006	4.8959	4.7
1951517	5.4853	5.4836	1.7

TABLE II

CURVE	FLUORESCER	OPERATING VOLTAGE (KV)	TIME INTERVAL
A	Cu	40	62 secs
B	Mo	60	93 secs
C	Tb	75	116 secs

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FIGURE CAPTIONS

Fig. 1. System flow chart showing the distribution of the membrane filters to the sampling sites and their subsequent retreival and analysis.

Fig. 2. Diagram of a conventional impactor illustrating the departure of massive particle trajectories from the streamline flow.

Fig. 3. Diagram of a single jet virtual impactor showing relevant dimensions.

Fig. 4. Cross section of final impactor design. The outside dimension of the upper flange is about 12 cm.

Fig. 5. Efficiency and loss curves for the final impactor design. A/A+B is the fraction of particles deposited on filter A divided by the total amount of particles collected.

Fig. 6. Schematic drawing of mechanical sampling changer and vacuum manifold.

Fig. 7. Idealized beta-spectrum with end-point energy = E_{MAX}. Shaded portion represents the number of events recorded above threshold.

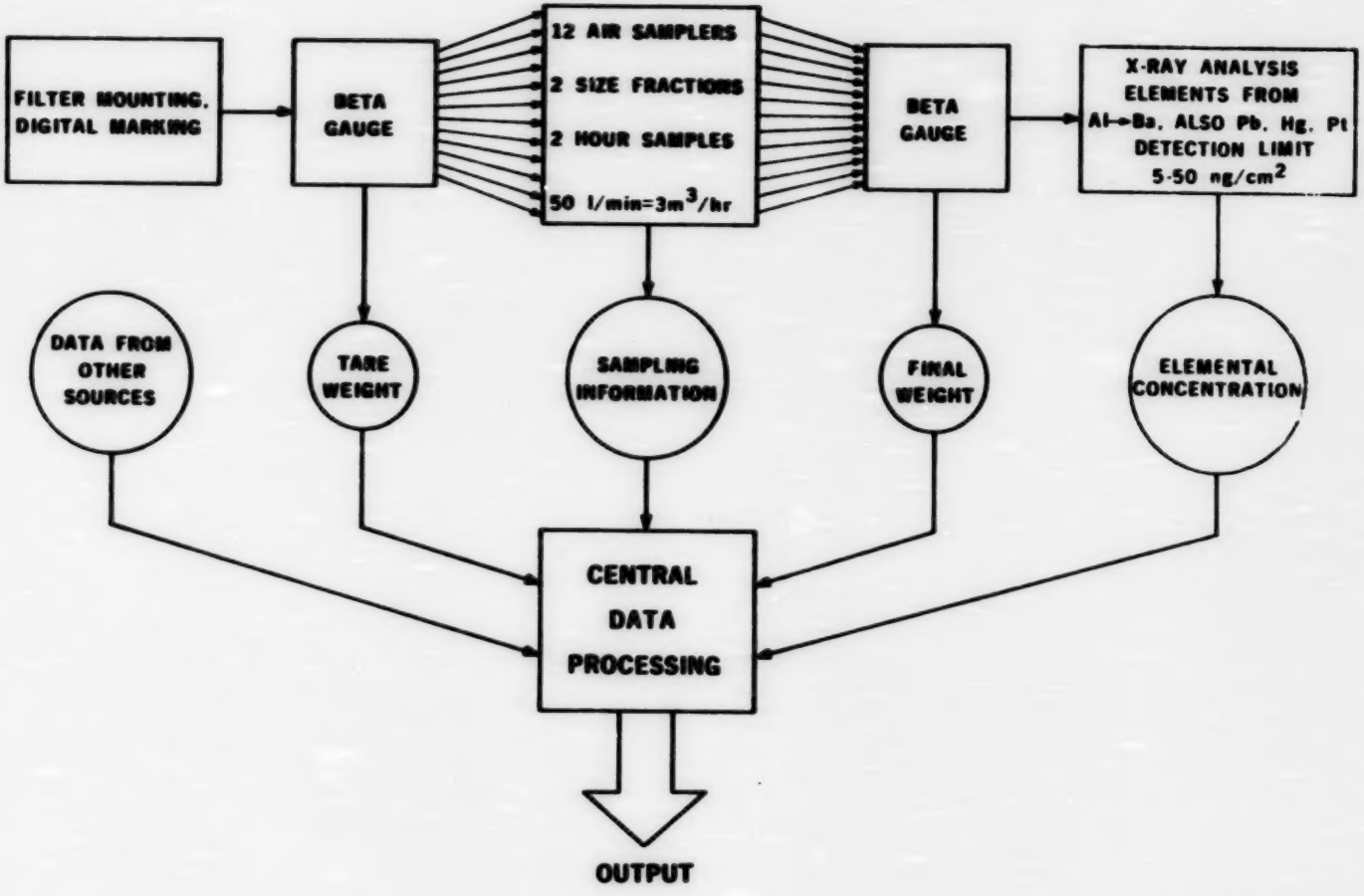
Fig. 8. Cross section of beta-gauge assembly.

Fig. 9. Calibration curves for the beta-gauge as a function of Z/A. Standards were thin films of Au, Pd, Ge and polycarbonate.

Fig. 10. Schematic of pulsed X-ray tube system.

Fig. 11. Plot of X-ray tube power and counting rate as a function of sample mass for the pulsed system.

Fig. 12. Detectability (3 σ) limits for the pulsed tube operated in the standard secondary fluorescence mode. Secondary targets were Tb, Mo and Cu.



XBL 743-538

Fig. 1

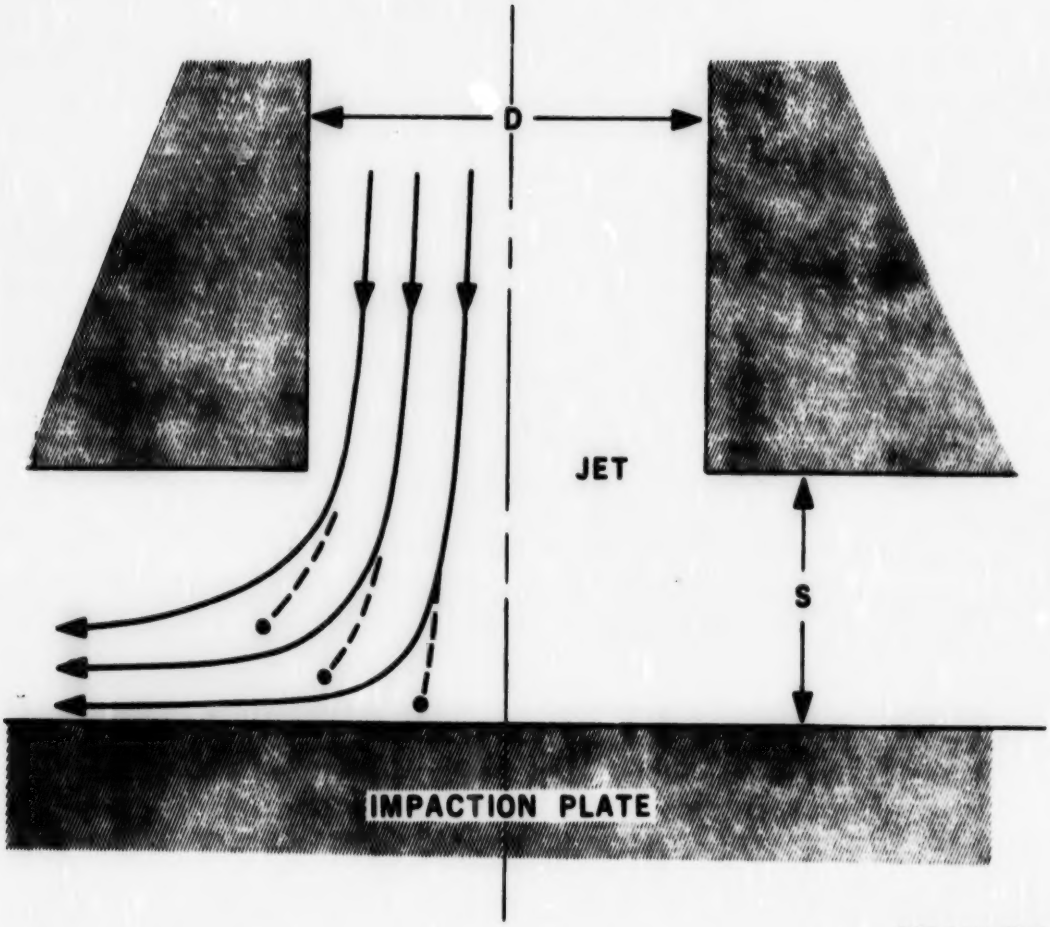
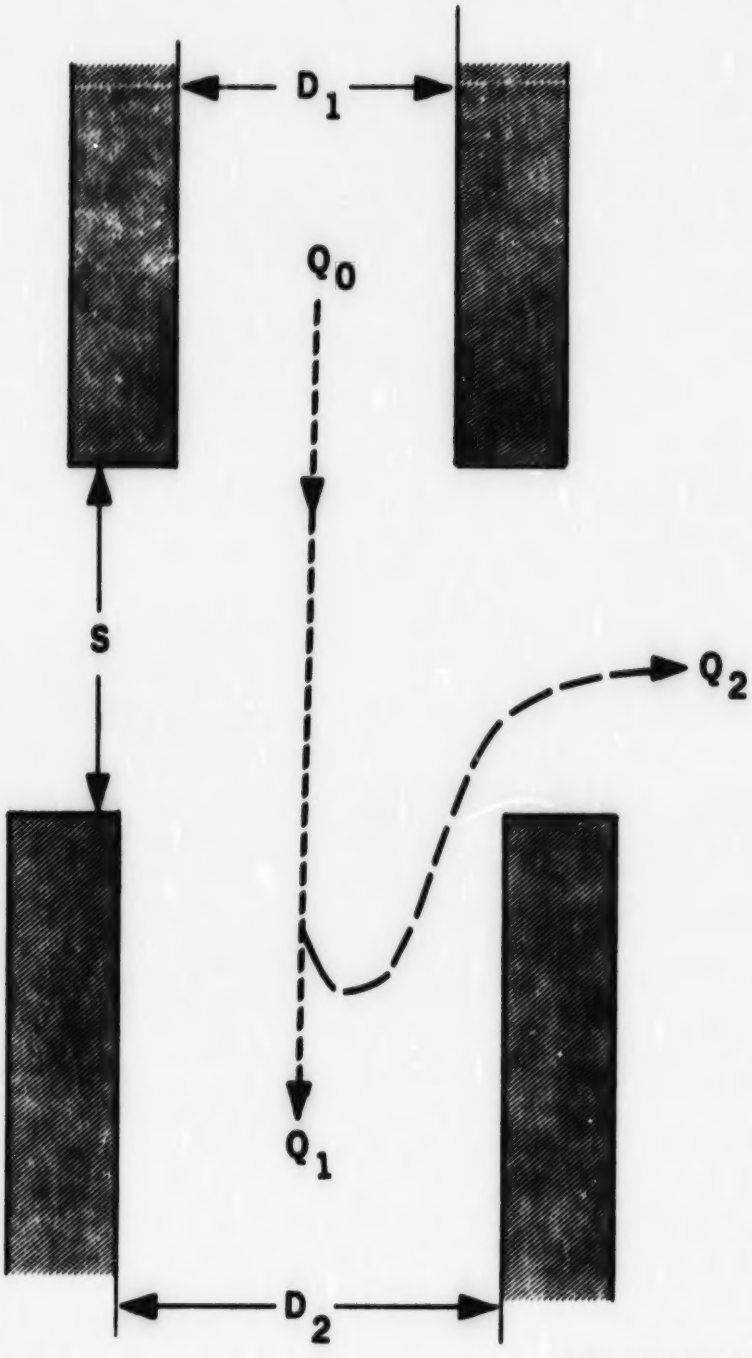


Fig. 2



XBL 7411-8542

Fig. 3

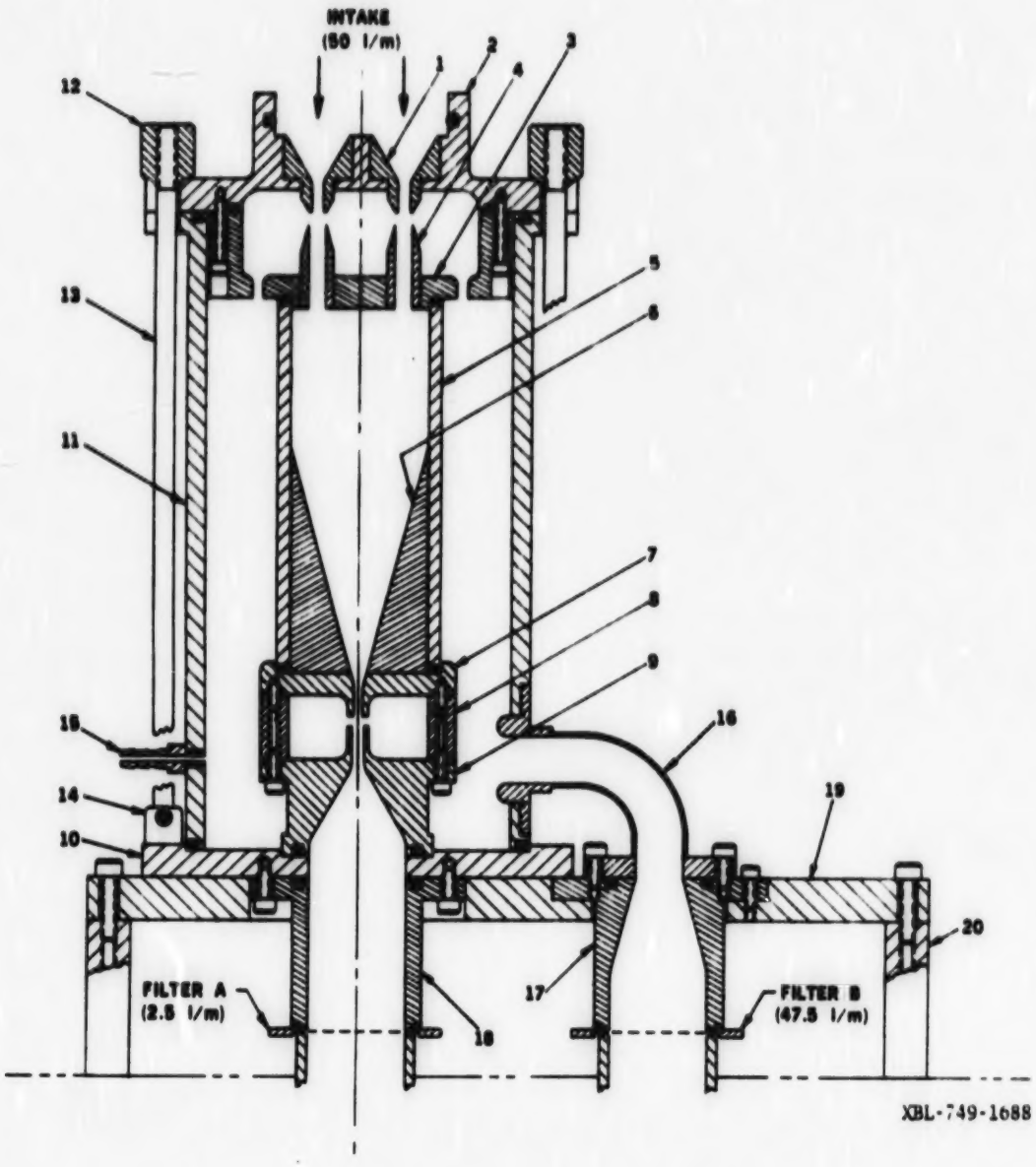
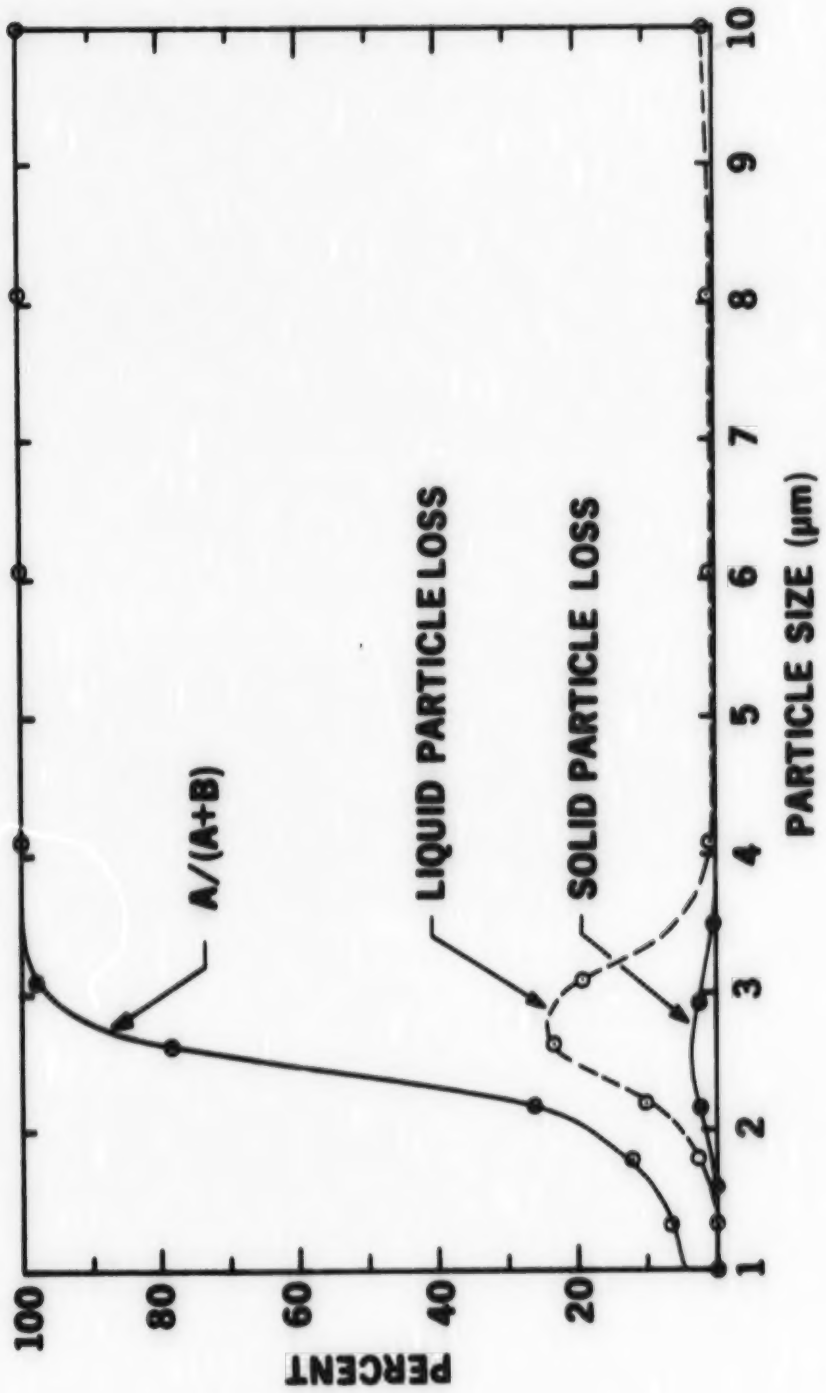

INTAKE
(50 l/m)
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
FILTER A
(2.5 l/m)
FILTER B
(47.5 l/m)
XBL-749-1688

Fig. 4



XBL 731-124

Fig. 5

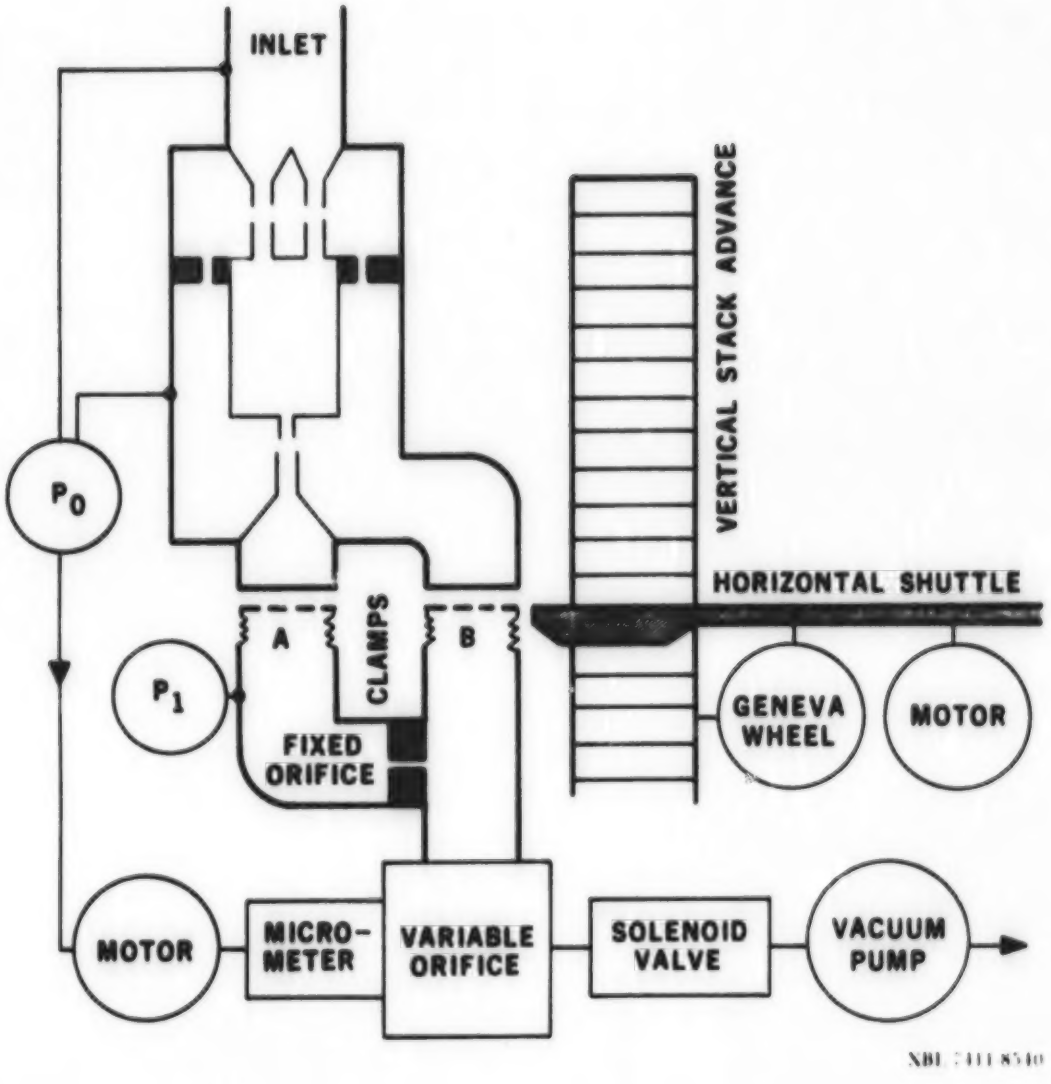

INLET
VERTICAL STACK ADVANCE
HORIZONTAL SHUTTLE
P_0
P_1
A
CLAMPS
B
FIXED ORIFICE
GENEVA WHEEL
MOTOR
MOTOR
MICRO-METER
VARIABLE ORIFICE
SOLENOID VALVE
VACUUM PUMP
NBL 7411-8540

Fig. 6

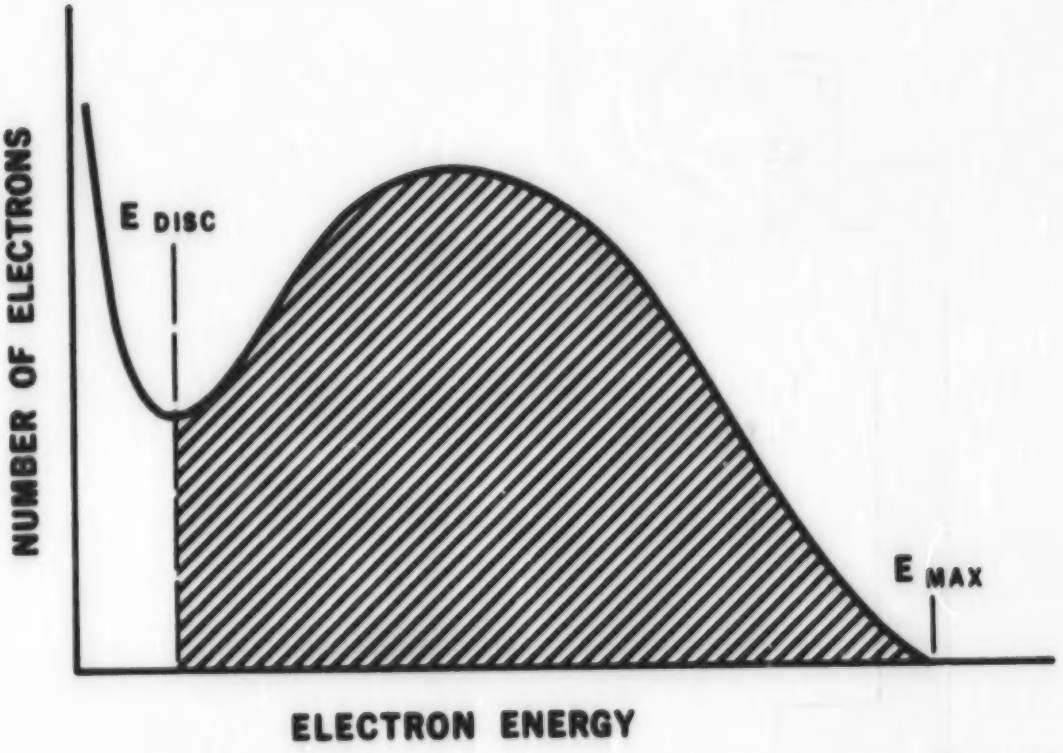


Fig. 7

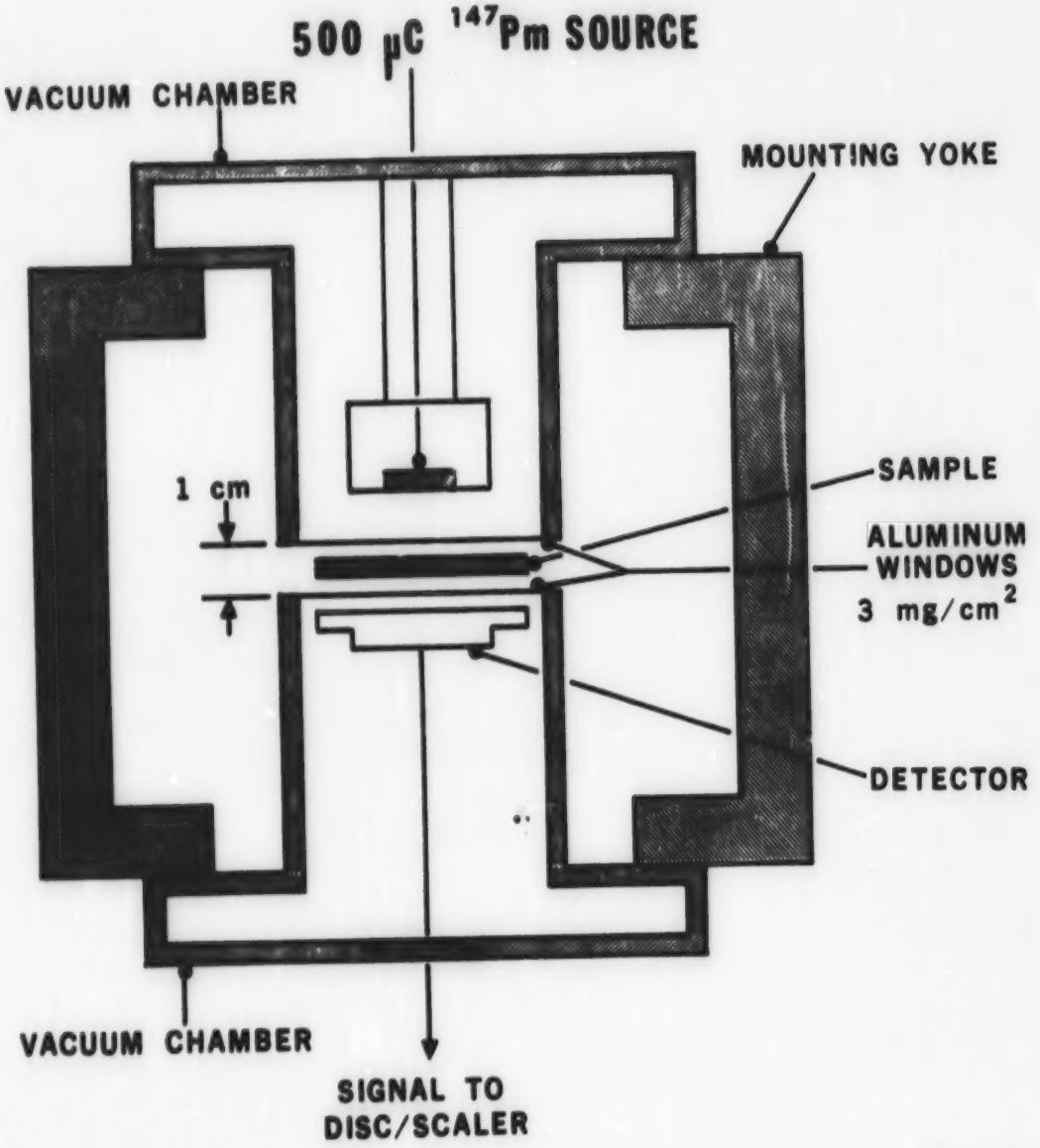
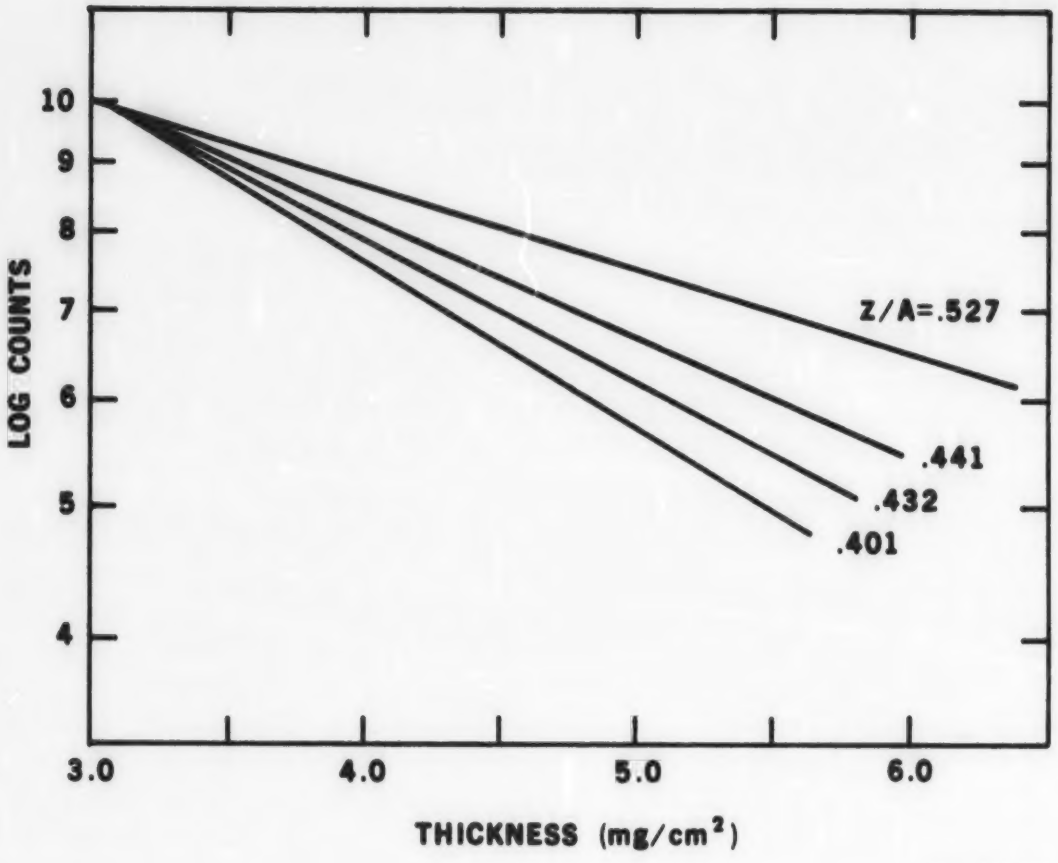

500 μC ^{147}Pm SOURCE
VACUUM CHAMBER
MOUNTING YOKE
1 cm
SAMPLE
ALUMINUM WINDOWS
3 mg/cm^2
DETECTOR
VACUUM CHAMBER
SIGNAL TO DISC/SCALER
XBL 752-327

Fig. 8



XBL 753-635

Fig. 9

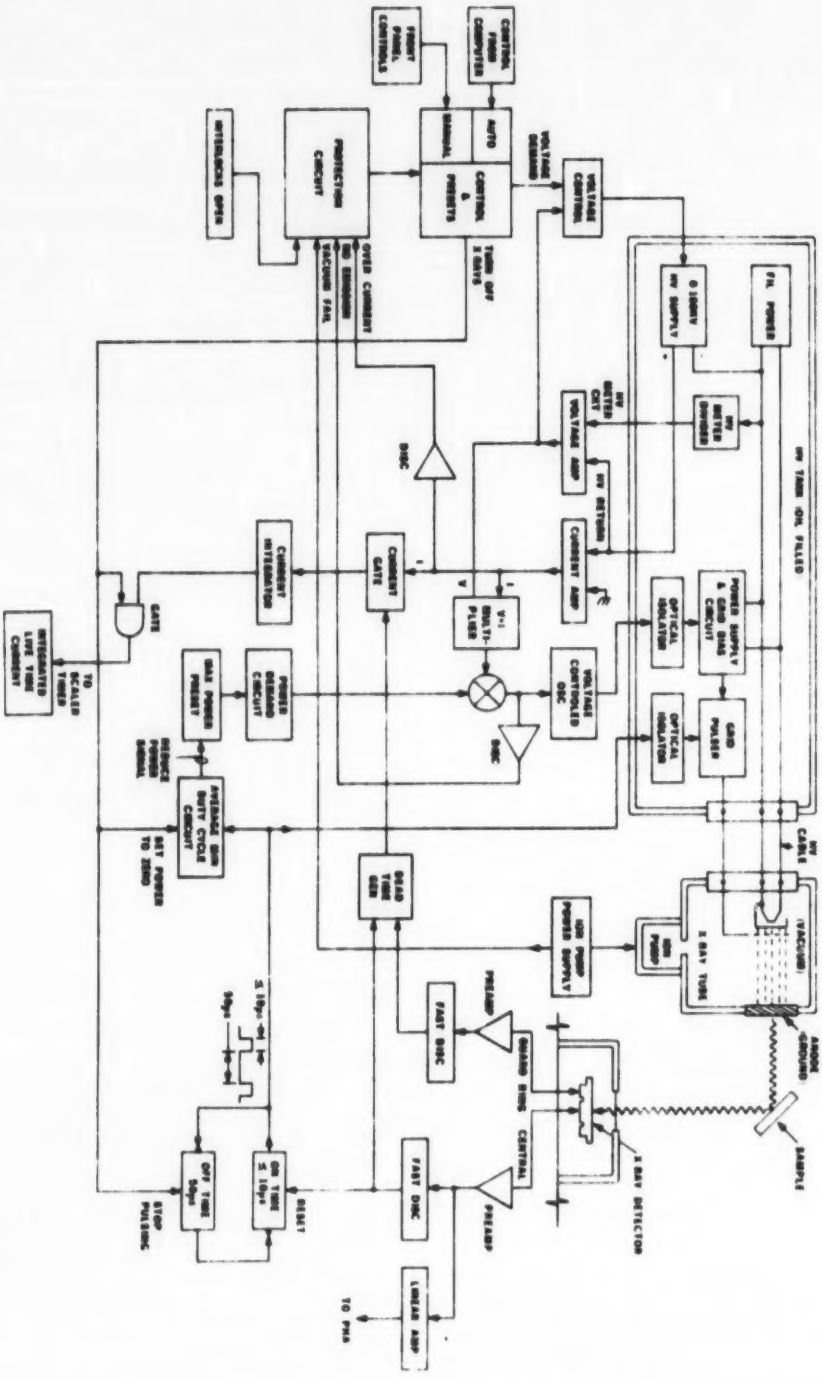

CONTROL ROOM COMPUTER
FRONT PANEL CONTROLS
AUTO
MANUAL
CONTROL & PRESETS
INTERLOCKS OPEN
PROTECTION CIRCUIT
VOLTAGE SELECT
VOLTAGE CONTROL
OVER CURRENT
TURN OFF 3 GATES
HV METER CKT
VOLTAGE AMP
HV METER DIVIDER
HV RETURN
CURRENT AMP
DISC
CURRENT INTEGRATOR
CURRENT GATE
V-I MULTIPLIER
GATE
INTEGRATED LIVE TIME CURRENT
TO SCALER TIMER
MAX POWER PRESET
POWER DEMAND CIRCUIT
VOLTAGE CONTROLLED OSC
REDUCE POWER SIGNAL
AVERAGE DUTY CYCLE CIRCUIT
SET POWER TO ZERO
DEAD TIME GEN
FIL POWER
HV TANK OIL FILLED
POWER SUPPLY & GRID BIAS CIRCUIT
OPTICAL ISOLATOR
GRID PULSER
HV CABLE
ION PUMP POWER SUPPLY
ION PUMP
X-RAY TUBE
ANODE GROUND
SAMPLE
PREAMP
FAST DISC
GUARD RING
CENTRAL
X-RAY DETECTOR
OFF TIME 50μs
ON TIME ≤ 10μs
DELAY
STOP PULSING
LINEAR AMP
TO PHA

Fig. 10

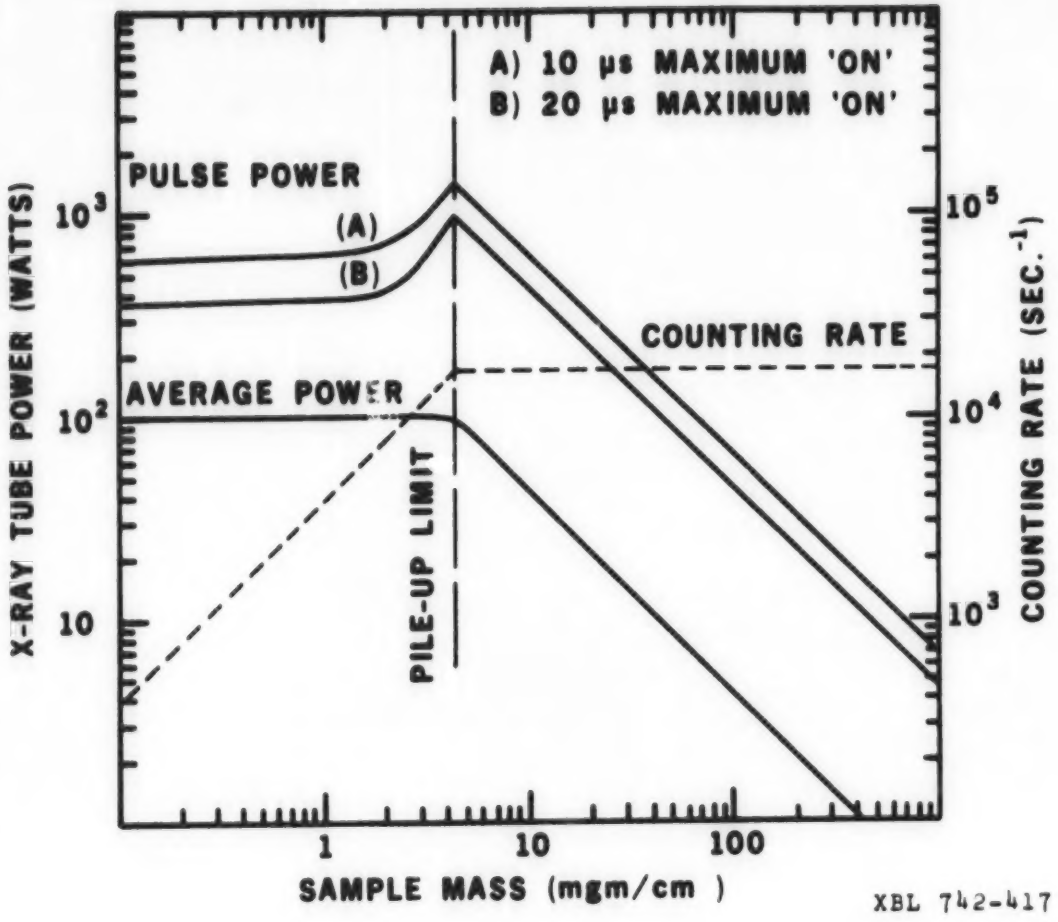
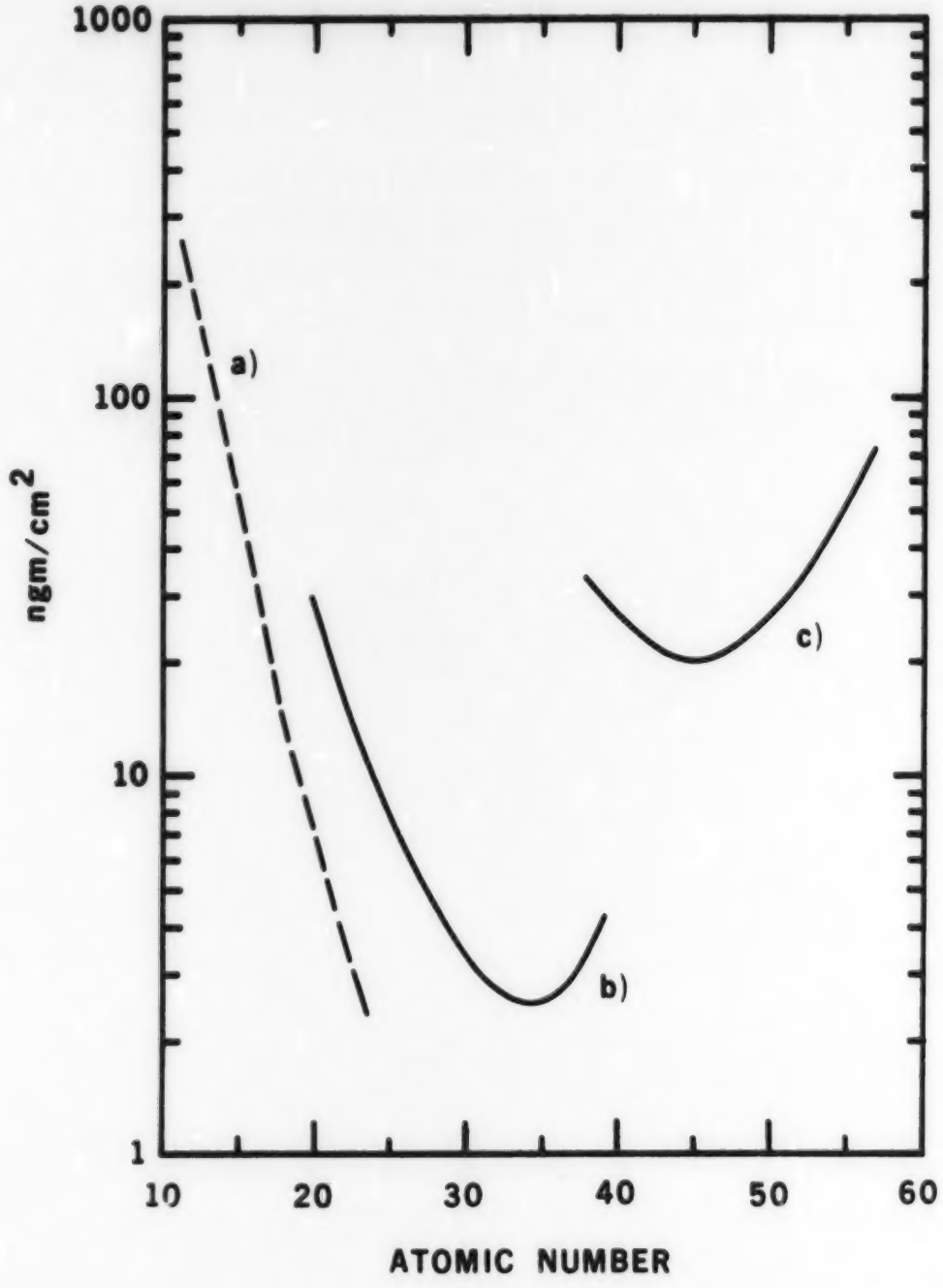

A) 10 μs MAXIMUM 'ON'
B) 20 μs MAXIMUM 'ON'
PULSE POWER
(A)
(B)
AVERAGE POWER
COUNTING RATE
PILE-UP LIMIT
X-RAY TUBE POWER (WATTS)
COUNTING RATE (SEC.$^{-1}$)
10^3
10^2
10
10^5
10^4
10^3
1
10
100
SAMPLE MASS (mgm/cm)
XBL 742-417

Fig. 11



XBL 753-694

Fig. 12